BIOCATALYTIC CONVERSION OF CRUDES: POSSIBLE PATHWAYS

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INTRODUCTION

Petroleum is a complex mixture of natural products which, under geological conditions (temperature, pressure, folding, migration and others), are subjected to multiple chemical, biochemical and physical reactions (1). Evolution of petroleum over geological periods of time leads to the formation of mixtures of hydrocarbons with different molecular weights and concentrations of saturates, aromatics, resins, asphaltenes and organometallics. Thus, low °API (<20) gravity oils are low in gasoline and high in residuum, i.e., as oils becomes heavier, the H/C ratios decrease, the NSO/C ratios increase and the oil becomes richer in asphaltenes and (2) Treatment of such complex mixtures with biocatalysts introduced under controlled conditions leads to bioconversion of crude oils via multiple inter- and intra-molecular chemical and biochemical processes. Some of the mechanistic aspects of such processes will be discussed.

Chemical reactions leading to the formation of different types of oils are influenced by the composition of the initial mix of natural products, their mutual interaction involving multiple reactive sites and the effects of chemical, biochemical and geological factors acting on the mixture (2,3). In spite of the chemical complexity of crude oils they can all be characterized and placed into distinct groups ranging from lights oils (°API >30) to heavy oils (°API <20). They are further distinguished by a number of chemical markers, compounds characteristic of major components of crudes which are different hydrocarbons, grouped according to their particular chemical structures: saturates, aromatics, resins and asphaltenes. Additional chemical characterization of oils distinguishes complex hydrocarbon mixtures by the relative concentration of compounds containing nitrogen, sulfur, oxygen and trace metals. The representative uniqueness of chemical markers has allowed to follow the chemical alterations in crude oils under reservoir as well as chemical and biochemical processing conditions (4-7). The latter is of particular importance in the studies dealing with biocatalytic conversion of heavy crude oils (e.g., Ref. 7). It has been shown by extensive use of chemical markers, that biochemical catalysts do not biodegrade, but rather, bioconvert heavy crudes to products with lower contents of sulfur, nitrogen and trace metals (7,8). Further, the extent and the specificity of bioconversion depends on the biocatalyst used and the chemical properties of the crude used, for example the difference between a heavy immature and a heavy biodegraded crude oil. Some aspects of the above observations will be briefly discussed in the present paper.

EXPERIMENTAL

Methods and procedures have been discussed in detail elsewhere (e.g, 7,9) and will be summarized in this section. .1. Biocatalyst and oil treatment: biocatalysts were prepared from the stock BNL collection and stirred into the reaction mixture containing the oil and nutrients and then extracted with methylene chloride; .2. gas chromatography/mass-spectrometry: the analyses were carried out with a Perkin Elmer Model 8700 gas chromatograph equipped with flame photometric detector (FPD) and a Finnigan ion trap mass spectrometer (ITD) for simultaneous analyses (GC-FPD/MS); .3. pyrolysis-gas chromatography-mass spectrometer (Py-GC-MS) utilized a Chemical Data System, Inc. (CDC) model 190 pyroprobe interfaced with GC-FPD-MS system as in .2.; .4. for nitrogen analyses appropriate nitrogen specific (nitrogen, phosphorous detector, PFPD) was used; .5. metals analyses were performed with a VG-induced-coupled-mass spectrometer (ICP-MS); .6. Saturate Aromatic, Resins and Asphaltene (SARA) analyses were carried out using a thin layer Chromatograph-Flame Ionization Detector (TLC-FID) and Chromatotron Model TH-10 of IATROSCANCO, using the rotating disc TLC-FID method (10) and .7. asphaltenes were precipitated with n-pentane from a methylene chloride solution.

RESULTS AND DISCUSSION

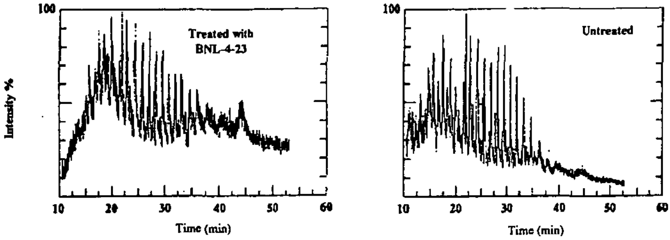
Experimental results to date suggest that a biocatalyst reacts at the active sites of polar molecules within the colloidal, micellar molecular solutions representative of three dimensional structures of crudes (7-14). It is the three dimensional structure of crudes as well as the chemical composition and the molecular structures of major constituents of oil that influence the reactivities of crude oils (15, 16). It has been known for some time (14) that measurement of one gross parameter (e.g., sulfur) in analyses of catalytically converted oils, for example hydrodesulfurization and hydrodemetalization is insufficient, and may lead to erroneous conclusions. Current experience suggests that similar oil characterization scenarios apply to biocatalytically converted oils. For example, the action of a single biocatalyst, BNL-4-23 on three, chemically different oils is summarized in Table 1. Monterey 851 is a heavy, California (onshore) biodegraded oil. OSC is an immature (offshore) biodegraded oil, while MWS, Midway Sunset is a steam treated heavy crude. There is a significant variation in the effects of a single biocatalyst on eight different parameters. Similar variations have been also observed where several different biocatalysts have been used on a single oil (examples in Refs. 6,7 and others). Further, the distribution of compounds containing active sites, i.e., heteroatoms, varies in concentration throughout different types of oils, where the three dimensional structure of oils allows for formation of bridges, clathrates, inclusion complexes and clusters which, chemically represent a reaction substrate eminently suitable for multiple and simultaneous reactions. The importance of initial reactivity at active sites has led to a set of experiments described in detail elsewhere (6-9) and will be for the purpose of this discussion, summarized briefly in Figure 1. In the analyses shown in Figure 1, experimental conditions for all the samples were kept constant in each case, so that a direct comparison of spectral results is possible. These results show that significant changes also occur in the n-pentane precipitated fractions (asphaltanes) which are not detected in the analyses of the whole oil. The chemical changes which lead to reaction mixtures analyzing as shown in Figures 1c, d, g, h indicate a break down in high molecular weight fractions. The multiple parameter analysis shows lowering in total sulfur concentration and also indicates a significant re-distribution of hydrocarbons.

The usefullness and importance of multiple parameter analysis as it relates to an understanding of fundamental mechanisms by which biocatalysis occurs as well as to its effects and efficiency is further illustrated by the following examples. Table 2 lists data for several fractions of different oils with their corresponding Conradson Carbon Residue (CCR) values. When CCR values are plotted against % of resins + asphaltenes, a decrease in the concentration of resins and asphaltenes also indicates a decrease in the Conradson Carbon value, an important consideration in refining of crudes, i.e., coking processes. The effect of biocatalytic conversion of OSC and MWS follows the same trend, however, biocatalysis accomplishes this at a much lower temperature and pressure compared to conventional refining. This very important experimental observation could not have been detected without multiple parameter analyses and systematic studies of chemical/biochemical mechanisms associated with biocatalysis.

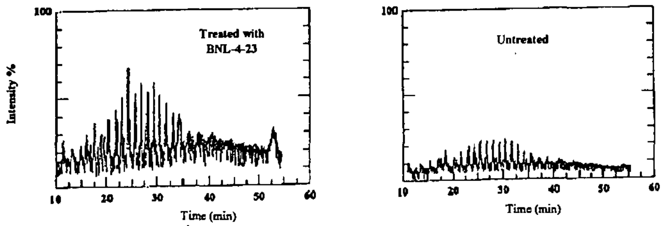
Table 1.
Characterization of Representative Biotreated Crude Oils

Oil	Monterey 851		OSC		MWS	
	%UN*	% TR** BNL-23	%UN	% TR BNL-23	%UN	% TR BNL-23
S	1.84	1.29 (-30)	4.4	2.42 (-45)	1.00	0.50 (-50)
N	0.59	0.44 (-25)	0.66	0.36 (-45)	0.79	0.63 (-20)
Ni	259 ppm	207 (-20)	80 ppm	64 (-20)	63 ppm	47 ppm (-25)
V	369 ppm	288 (-22)	22 ppm	18.5 (-16)	24 ppm	15.9 ppm (-36)
SAT %	19.2	34.4	17.3	51.6	19.2	66.3
AROM %	45.2	29.7	39.1	20.5	44.9	11.2
RESIN %	31.2	32.7	37.1	22.3	35.3	19.3
ASPH %	4.4	3.6	6.2	5.7	2.60	3.1

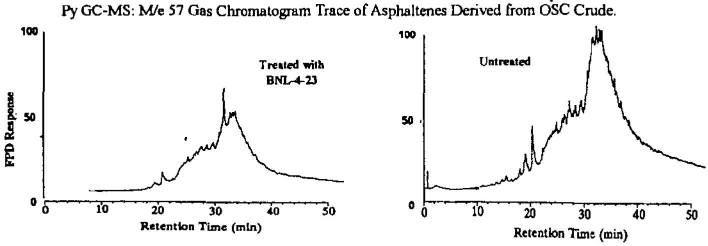
* UN = untreated
**TR = treated
(-) = % reduction



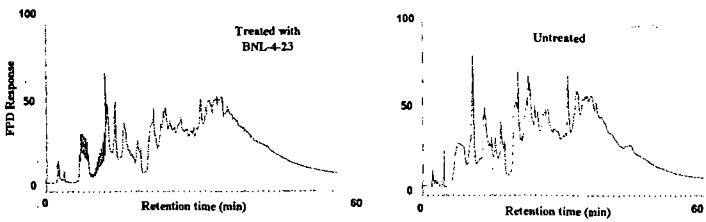
GC-MS Analysis: M/e 57 Gas Chromatogram Trace of Untreated and Treated OSC Crude.



Py GC-MS: M/e 57 Gas Chromatogram Trace of Asphaltenes Derived from OSC Crude.



FPD (Sulfur Specific Detector) Chromatogram Trace of Untreated and Treated OSC Crude.



Pyrolysis-gas Chromatograph Analysis (Py-GC) FPD (Sulfur Specific Detector) Trace of Asphaltenes from OSC Crude Treated with BNL-4-23

Figure 1. Multiple Parameter Analysis of Oils.

Table 2.
Distribution of Fractions and Residues in Representative Oils

Reference		Asphaltenes	Resins	Res+Asph.	Carbon residue
2	Light Alberta	0.2	9.4	9.6	1.3
2	crudes	0.1	11.6	11.7	2.6
2	for comparison	0.9	12.2	13.1	2.9
2		0.3	13.0	13.3	3.0
17	Daquig	0	29.9	29.9	8.5
15	Gach Saran	6.8	28.5	35.3	8.8
2	Boscan	11.9	24.1	36.0	10.4
15	Heavy Arabian	12.6	27.5	40.1	12.6
2	Cold Lake	15.7	28.7	44.4	13.6
17	Shenghi	45.7	1.6	47.3	12.7
15	Blend	11.4	36.0	47.4	11.0
2	Bermudez Lake	35.3	14.4	49.7	13.4
2	Athabasca	16.9	34.1	51.0	18.5
15	Maya	25.2	25.9	51.1	15.3
2	Lloydminister	12.9	38.4	51.3	11.8
17	Renqiu	0	53.1	53.1	18.6
15	Hondo	13.9	40.2	54.1	10.8
2	Qayarah	20.4	36.1	56.5	15.6
2	Trinidad Lake	33.3	29.4	62.7	10.8

2-Speight
14-Dolbear, Tang and Moorhead
16-Chan and Luoyan

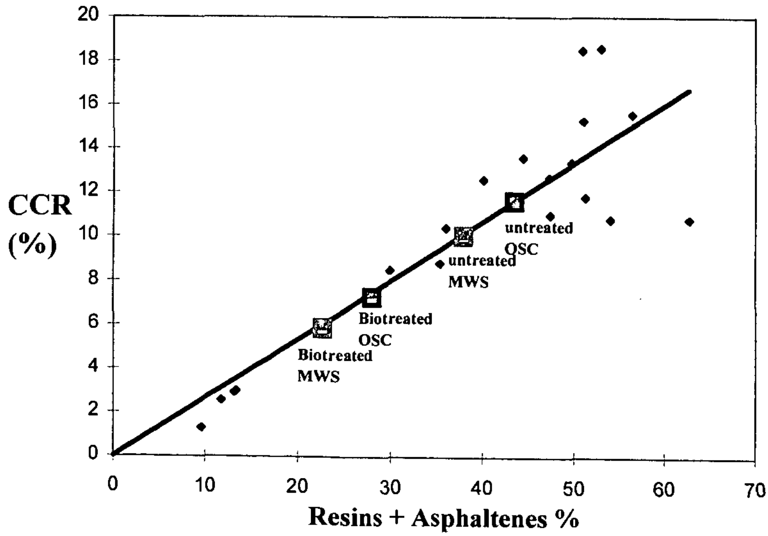


Figure 2. Conradson Carbon Residue (CCR) as a function of the Resin + Asphaltene Fraction

CONCLUSIONS

Multiple chemical changes which occur during biocatalysis of heavy crude oils are due to complex inter- and intra-molecular reactions. These reactions follow distinct trends which can be followed by a set of chemical markers associated with major heavy crude oil fractions. Experience gained with chemical catalytic conversion of crudes, shows that properties described by a single paramter only (e.g., sulfur) are not in themselves good predictors of catalytic processing. The data currently available for biocatalytic conversion of heavy crudes appear to be consistent with those of chemical catalysis and require an array of chemical markers in evaluation of biocatalytic effects.

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